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Elipsometric Investigations of Nano Thickness $Cu_2ZnSnSe_4$ Films

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Abstract

An ellipsometric research of a thin layer of $Cu_2ZnSnSe_4$ with a thickness of approximately 100 nm obtained on a glass substrate by the method of magnetron sputtering of a target with a diameter of 10 cm made by pressing from the crushed nanopowder of the $Cu_2ZnSnSe_4$ crystal was carried out. The experimental results are in good agreement with the ε-spectrum calculated within the GW quasi-particle approximation, and the possible origin of the identified high-energy features is identified. Magnetron sputtering occurs during a gas discharge with a voltage of ~ 300 - 600 V and a current of ~ (3-5) A. SE measurements were performed using an angled spectroscopic ellipsometer (J.A. Woollam VASE) at room temperature. Ellipsometric parameters were obtained in the photon energy range (1.03 to 6.4 eV) and at 65^0. The pseudo dielectric functions were mathematically modeled and then the energy dependence graphs of the dielectric functions (ε_1 and ε_2) were constructed. Here n - the real part of the refractive index k - and the imaginary part, that is, the extinction coefficient. Based on the relationship between the dielectric functions and the refractive index, the values of the dielectric functions were taken into account in the formula, and the values of the real part of the refractive index and the extinction coefficient were determined. That is, in the $Cu_2ZnSnSe_4$ thin film, E_g=1.6 eV, and high energy features are determined at energies of 4 eV and 4.6 eV.

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1. Introduction

As is known from the scientific literature, solar cells on Cu $(In,Ga)Se_2$ (CIGSe) have greater efficiency of than 20%. However, elements such as indium and tellurium are rare in nature, and Cd is highly toxic, which can limit the use of such devices at the terawatt scale. Last times, it has been established that Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) and $Cu_2ZnSn(S, Se)_4$ (CZTSSe) are non-toxic substances and are considered to have promising optoelectronic properties. At the same time, these substances are considered to be among the substances that have begun to replace thin-film photovoltaic materials widely used on Earth based on silicon and materials with chalcopyrite crystal structures.

The idea of Cu_2ZnSnS_4 (CZTS) thin film based solar cells consists of the bottom principles. Such complex semiconductor photovoltaic cells satisfy two essential conditions within a certain optimum range:

1. The first principe is the direct nature of the band gap
2. And the second is width of the band gap

Because the first factor of the absorption coefficient for the Cu_2ZnSnS_4 thin film is quite large, a film only micron thick absorbs enough sunlight and has no harmful effects on photocurrents when used as an absorber. In the obtained film, the radiative recombination probability is greater than probability of non-radiative recombination if there is both absorption and emission for photons, due to the permitted direct transfer of carriers between the valence band and the conduction band without crystal defects and any coupling similar to phonons.

There are major differences between Copper based fourth group elements and group III-V and II-VI binary semiconductors. Firstly conventional semiconductors have sp^3 hybridization. The secondly, group III-V, group II-VI semiconductor cations have three or two s valence electrons. These properties indicate that the Cu- Copper vacancy energy of formation - V_{Cu} is small compared to the energy for the corresponding cation vacancies formed in conventional semiconductors. Therefore, it is relatively easy to grow highly non-stoichiometric materials with natural defects based on Copper. Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ have energies $Eg \approx 1.2 - 0.9$ eV, respectively.

Cu_2ZnSnS_4 (CZTS) has a coefficient of high absorption above 10^4 cm^{-1} and an optical band gap energy of (1.4–1.5) eV, all these make it a promising material for application in thin-film solar cell devices. As for the devices created on the basis of the Cu_2ZnSnS_4 based solar cell, a conversion efficiency of 8.4% was achieved. This value leads to a record efficiency of 12.6% even in $Cu_2ZnSn(S,Se)_4$ compounds with corresponding selenium content.

2. Thin Layer Preparation and Methodology of Experiments.

2.1. Thin Films Technology Methods

Thin films of $Cu_2ZnSnSe_4$ (CZTSe) were deposited on an optical glass substrate in argon gas atmosphere in a modified UVN-71P vacuum setup by magnetron sputtering method at room temperature.

Magnetron sputtering occurs during a gas discharge with a voltage of (300 - 600 V) and a current of (3-5) A. Ellipsometric research of the CZTSe thin film was carried out at room temperature by magnetron sputtering on a 20 mm x 20 mm glass substrate. SE - Scanning measurements were made using a spectroscopic ellipsometer "J.A.Woollam VASE" at room temperature. Note that the ellipsometric parameters were obtained in the photon energy range (1.03 to 6.4 eV) and at 65^0 angles.

The samples were obtained on a glass seat by the method of magnetron sputtering in the "Physics of Heterostructures" laboratory of the Institute of Physics. The thickness of the $Cu_2ZnSnSe_4$ thin layer on which ES studies were performed is approximately 100 nm.

3. Ellipsometric research of Thin Films of $Cu_2ZnSnSe_4$ Kieserite Structured Semiconductor Drawn on a Glass Substrate by Magnetron Sputtering Method.

3.1. Discussions of Results

Spectroscopic ellipsometry measurements were obtained using an angled spectroscopic ellipsometer ((J.A. Woollam VASE)) at room temperature. Ellipsometric parameters corresponding to the energy range of the photon "1.03 to 6.4 eV" and at 65^0 were obtained. After the procedure, the effect of oxides and side effects were minimized, deviations caused by additional effects were eliminated in the obtained results. Based on the obtained results, the pseudo dielectric functions were mathematically modelled and then the energy dependence graphs of the dielectric functions (ε_1 and ε_2) were constructed (Figure 1)

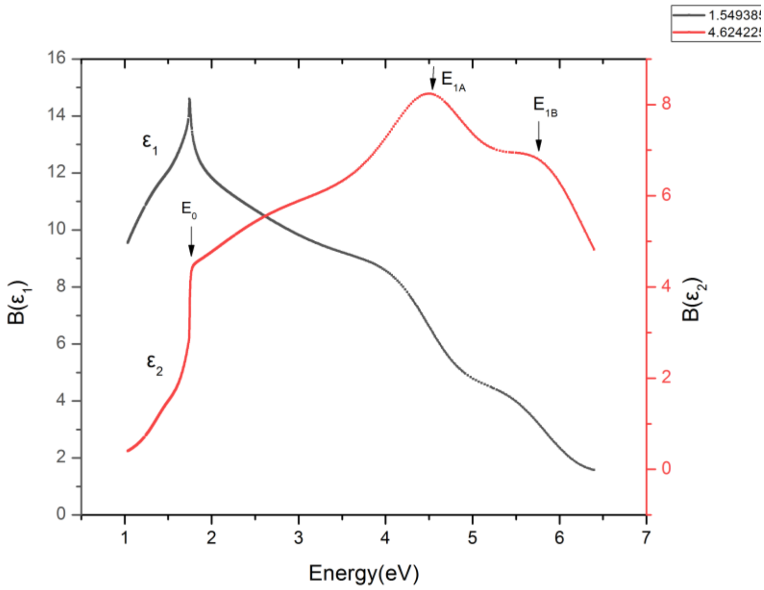

Figure 1. Energy dependence of dielectric functions ε_1 and ε_2 of $Cu_2ZnSnSe_4$-based thin film

"A simulated annealing" algorithm was used to calculate the "Adachi model" MDF parameters for the dielectric function. Using the SA algorithm, we can write the desired function by minimizing the MDF parameters [12, 13].

$$F = \sum_{i=1}^{N} \left(\left| \frac{\varepsilon_1(E_i)}{\varepsilon_1^{\text{expt}}(E_i)} - 1 \right| + \left| \frac{\varepsilon_2(E_i)}{\varepsilon_2^{\text{expt}}(E_i)} - 1 \right| \right)^2 \quad (1)$$

Here, $\varepsilon_1(E_i)$, $\varepsilon_1^{\text{expt}}(E_i)$, $\varepsilon_2(E_i)$, $\varepsilon_2^{\text{expt}}(E_i)$ are the real and imaginary parts of the experimentally calculated complex dielectric function, respectively. Here N is the number of experimental points.

As we know, the following relationship exists between dielectric functions and refractive index:

$$\varepsilon_1 + \varepsilon_2 i = N^2; \quad N = n + ik = [\varepsilon]^{\frac{1}{2}} \qquad (2)$$

Here "n" is the real part of the refractive index, "k" and the imaginary part, that is, the extinction coefficient. Based on the relationship between the dielectric functions and the refractive index, the values of the dielectric functions were taken into account in the formula, and at the same time the values of the real part of the refractive index and the value of the extinction coefficient were obtained.

As a result, their energy dependence graphs were constructed with the help of a special program (Figure 2.)

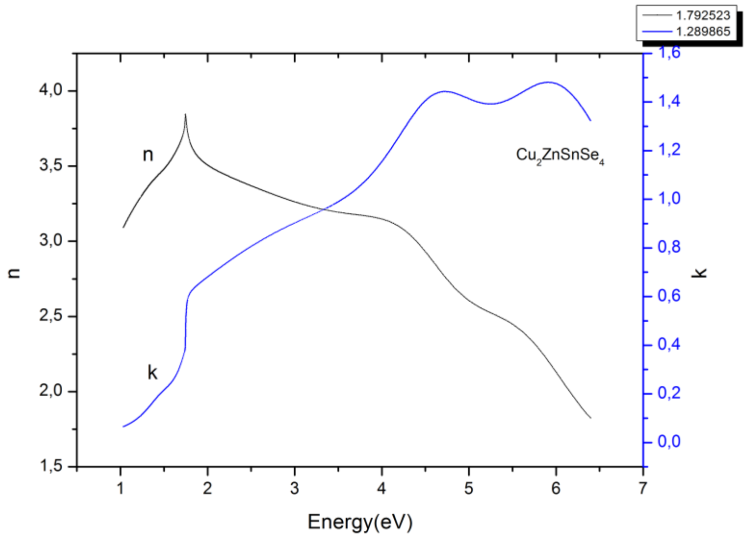

Figure 2. Energy dependence graphs of n and k in $Cu_2ZnSnSe_4$ thin film

In this graph, when we look at the results obtained from the graph of energy dependence of n - refractive index and k - extinction coefficient, we see that the results obtained from the graph are in agreement with our previous results for $Cu_2ZnSnSe_4$ thin film based on $Cu_2ZnSnSe_4$. That is, in the $Cu_2ZnSnSe_4$ thin film, E_g=1.6 eV, and high energy features are determined at energies of 4 eV and 4.6 eV.

4. Conclusion

- A thin layer of $Cu_2ZnSnSe_4$ was obtained using a magnetron sputtering method on a glass substrate in an argon gas environment.
- After the procedure, the effects of oxides and extraneous effects were minimized, and by eliminating the deviations caused by additional effects in the obtained results, mathematical modeling for pseudo dielectric functions was performed based on the results, and then the energy dependence graphs of the dielectric functions (ε_1 and ε_2) of thin $Cu_2ZnSnSe_4$ layers were constructed.
- As a result of SE measurements using a spectroscopic ellipsometer "J.A. Woollam VASE" in the energy range "1.03 to 6.4 eV" and at 65^0, the values of the values of the real part of the refractive index and the value of the extinction coefficient were obtained from the formula based on the relationship between the dielectric functions and the refractive index in thin $Cu_2ZnSnSe_4$ layers. As a result, their energy dependence graphs were constructed with the help of a special program.

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